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1. REPORT DATE (DD-MM-YYYY) 20-11-2014		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 31-Jan-2014 - 30-Oct-2014	
4. TITLE AND SUBTITLE Final Report: Chain Growth Cross Coupling Polymerizations Towards Chiral and Ladder Main Chain Polymers			5a. CONTRACT NUMBER W911NF-14-1-0062		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Yan Xia			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Stanford University 3160 Porter Drive, Suite 100  Palo Alto, CA 94304 -8445			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 64967-CH-II.1		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT We developed a new method to synthesize rigid ladder polymers using efficient, clean palladium catalyzed annulation reactions with low catalyst loading (1 mol%). Rigid ladder polymers with benzocyclobutene backbone linkages can be synthesized from copolymerization of readily accessible aryl dibromides and norbornadiene or polymerization of AB type monomers bearing norbornene and aryl bromide or triflate moieties. High molecular weight (10-40 kDa) rigid ladder polymers can be obtained with complete monomer conversions. Diverse monomers also gave different, fixed ladder polymer conformations. The ladder polymers exhibited excellent thermal stability.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Yan Xia
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 650-723-9059



## Report Title

Final Report: Chain Growth Cross Coupling Polymerizations Towards Chiral and Ladder Main Chain Polymers

### ABSTRACT

We developed a new method to synthesize rigid ladder polymers using efficient, clean palladium catalyzed annulation reactions with low catalyst loading (1 mol%). Rigid ladder polymers with benzocyclobutene backbone linkages can be synthesized from copolymerization of readily accessible aryl dibromides and norbornadiene or polymerization of AB type monomers bearing norbornene and aryl bromide or triflate moieties. High molecular weight (10-40 kDa) rigid ladder polymers can be obtained with complete monomer conversions. Diverse monomers also gave different, fixed ladder polymer conformations. The ladder polymers exhibited excellent thermal stability, high carbonization yield, and large intrinsic porosity.

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## Final Progress Report

### “Efficient Synthesis of Rigid Ladder Polymers”

Grant number: W911NF-14-1-0062 “Chain Growth Cross Coupling Polymerizations  
Towards Chiral and Ladder Main Chain Polymers”

#### Problem Studied

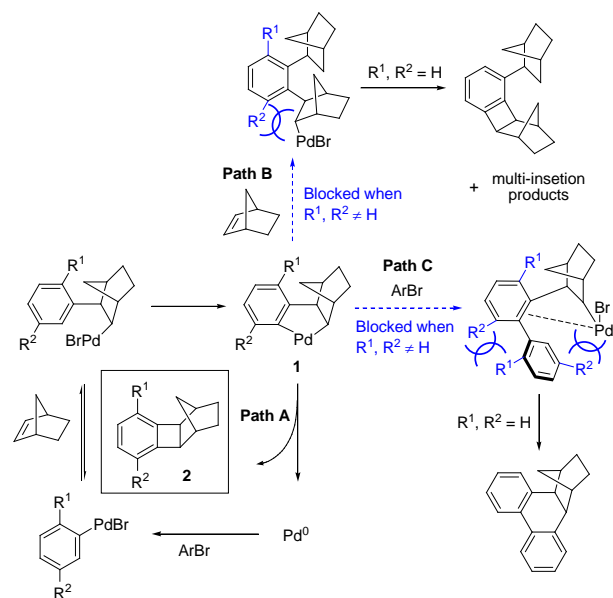
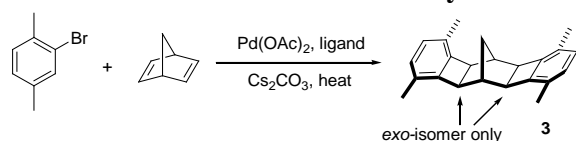
A central challenge in polymer chemistry is to precisely and efficiently control polymer architectures, which strongly influence the physical properties and applications of polymeric materials. In contrast to conventional polymers connected by single bonds, ladder polymers represent a unique architecture, where each repeat unit is connected by two bonds,<sup>1-2</sup> resulting in much more restricted chain conformations. Rigid ladder polymers have recently been shown to be very promising materials for efficient gas separation and the high rigidity was critical for selectivity in gas separation.<sup>3-4</sup> In addition to gas separation, we also envision a wide range of applications for rigid ladder polymers resulting from the high anisotropy and intrinsic porosity, including dielectric materials, porous solid support, and new precursors to nanostructured carbon materials. However, only two methods exist to synthesize ladder polymers by simultaneous formation of two-bond linkages. Schlüter and Swager groups pioneered the synthesis of ladder polymers via Diels-Alder reactions,<sup>5-7</sup> but the polymerizations required extremely high pressure (8800 atm) and/or high temperature (>170 °C). McKeown group recently developed ladder polymer synthesis based on Tröger’s base formation<sup>4,8</sup>. But multi-step monomer syntheses were required and no regio- or stereo-control could be achieved in the reported examples.

Our laboratory is interested in exploring powerful and versatile transition metal catalysis to synthesize novel polymers from readily accessible building blocks. Transition metal catalysis has continuously stimulated the emergence of new polymer chemistry to gain access to novel polymers and new materials.<sup>9-13</sup> During the tenure of this STIR funding, we have developed the first catalytic synthesis of rigid ladder polymers by clean and efficient Pd catalyzed annulation reaction. This new method provides exclusively rigid ladder polymer structures in nearly quantitative conversions from readily available norbornene and aryl bromide as the monomers.

#### Important Results

Catellani and coworkers explored Pd catalyzed reactions between aryl bromides and norbornene (NB).<sup>16</sup> A stable palladacycle **1** from C-H activation on the arene can be formed in the catalytic cycle, which can undergo reductive elimination to form an interesting benzocyclobutene (BCB) product **2**,<sup>17-20</sup> as well as undergo pathways **B** and **C**, leading to other products (Scheme 1).<sup>16</sup> We were intrigued by the BCB product and envisioned it as a novel motif to build rigid ladder polymers. However, exclusive selectivity and high efficiency for the annulation pathway is a prerequisite to utilize this reaction for polymer synthesis. Our first step was to design substrates and optimize conditions for exclusive BCB product formation. We hypothesized that blocking the 2,5-positions of the aryl halide may inhibit the reaction pathways **B** and **C** due to steric congestion and funnel all the formed palladacycle **1** to the desired BCB product.



**Scheme 1. Pd Catalyzed Annulation: Possible Products and Selectivity****Table 1. Optimization of a Model Reaction for Ladder Polymerization<sup>a</sup>**

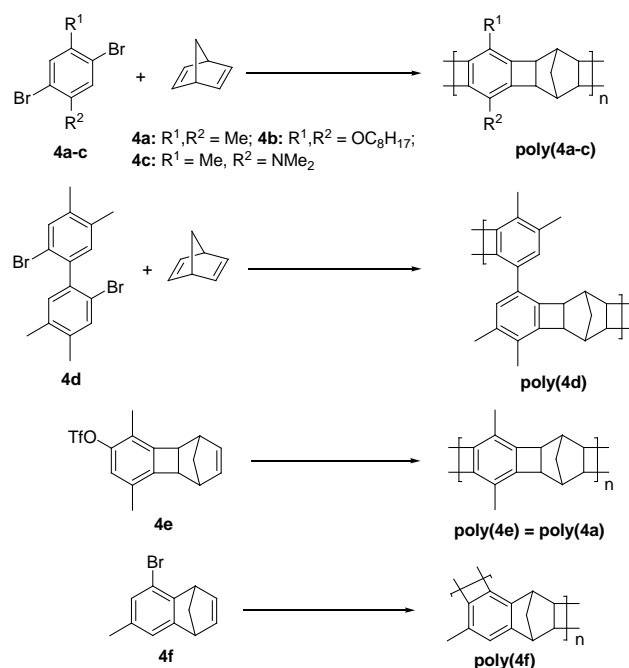
entry	ligand	temp. (°C)	cat. (mol %) <sup>b</sup>	conv. (%) <sup>c</sup>
1	PPh <sub>3</sub>	130	5	>98
2	PCy <sub>3</sub>	130	5	94
3	PtBu <sub>3</sub>	130	5	68
4	P( <i>o</i> -Tol) <sub>3</sub>	130	5	<5
5	NHC <sup>d</sup>	130	5	<5
6	PPh <sub>3</sub>	115	5	>98
7	PPh <sub>3</sub>	100	5	80
8	PPh <sub>3</sub>	115	1	>98
9 <sup>e</sup>	PPh <sub>3</sub>	115	0.1	91
10 <sup>f</sup>	PPh <sub>3</sub>	115	0.1	>98

<sup>a</sup>Reactions were performed using Pd(OAc)<sub>2</sub>, 2 eq. ligand to Pd, Cs<sub>2</sub>CO<sub>3</sub>, at [NBD] = 0.1 M in toluene for 5 h in a sealed tube, unless otherwise noted. <sup>b</sup>Based on the mole ratio of Pd to halide. <sup>c</sup>Determined by <sup>1</sup>H NMR of crude reaction mixture. <sup>d</sup>PEPPSI-IPr Pd catalyst used. <sup>e</sup>Reaction run for 24 h. <sup>f</sup>Reaction run in THF for 24 h.

Our initial attempt on a model reaction between 2-bromotoluene and norbornadiene (NBD) using 10 mol % Pd(PPh<sub>3</sub>)<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub> resulted in complete consumption of starting materials but led to complex product mixtures. To test our hypothesis of blocking reaction pathways **B** and **C**, we started with commercially available 2,5-dimethyl-bromobenzene and NBD. Gratifyingly, after initial optimization, the desired BCB **3** product was cleanly formed in >98% conversion using Pd(OAc)<sub>2</sub>, PPh<sub>3</sub>, and Cs<sub>2</sub>CO<sub>3</sub> at 130 °C, and the reaction was highly stereoselective with exclusively the *exo*-isomer formed, as indicated by the NOE experiment. The reaction was sensitive to the sterics of the phosphine ligand as bulkier ligands gave lower conversions (Table 1, entry 3-4). *N*-heterocyclic carbene (NHC) based PEPPSI catalyst, although highly efficient in many cross-coupling reactions, gave very low conversion (Table 1, entry 5). Surprisingly, under optimized conditions, we could lower the catalyst loading to only 0.1 mol % and reaction temperature to 115 °C and still obtained 91% and complete conversions to **3** in toluene and THF, respectively, after 24 h. The turnover number (TON) was measured to be 1176 and turnover frequency (TOF) to be 49 h<sup>-1</sup>. 0.1 mol% Pd represents nearly two orders of magnitude reduction in catalyst loading as compared to annulation reactions using other substrates and conditions reported by Catellani and Lautens groups.<sup>18-20</sup> The low catalyst loading and clean chemistry open the door for the application of this annulation reaction to polymer chemistry and scalable materials synthesis.

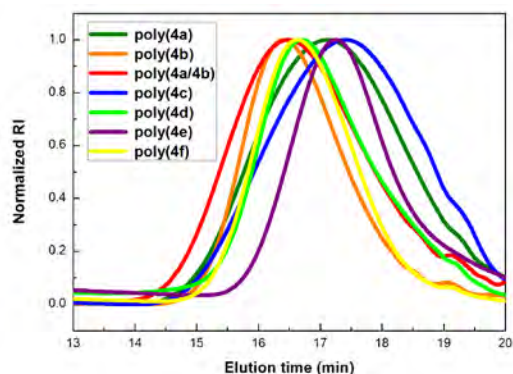
We next proceeded with polymerization of NBD and various aryl dibromides (Table 2). Polymers were obtained with complete monomer conversions for attempted aryl dibromides **4a-d**. The resulting ladder polymers can be dissolved in THF and their absolute MW was measured by gel permeation chromatography (GPC) coupled with a multi-angle laser light scattering (MALLS) detector. The efficient polymerization resulted in ladder polymers with high MWs in the range of 10-40 kDa and relatively narrow, mono-modal MW distribution (Table 2 and Figure 1). The high MW and relatively low PDI are particularly gratifying since the polymerization is presumably step-growth polymerization.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy indicated exclusive BCB ladder backbone linkage and the expected end group signals of the olefin from NB and of the arene protons from aryl bromide and debrominated arene (Figure 2). The resulting ladder polymers are generally soluble in nonpolar solvents, such as THF, DCM, and chloroform. Uniquely, the straight BCB linkage keeps the backbone of **poly(4a-c)** in a bowing-ribbon conformation (Figure 3). The overall polymer chain may resemble a disc shape, which we plan to study in future scattering experiments. The biphenyl monomer **4d** represents one type of easily accessible monomers that can give the resulting ladder polymers a certain degree of bending freedom in two dimensions resulting from the restricted biphenyl bond (Figure 3). Furthermore, these polymers can be synthesized on gram scale thanks to the facile access to a large number of aryl bromides, paving the way for their materials applications.

**Table 2. Synthesis of Various Benzocyclobutene Ladder Polymers**

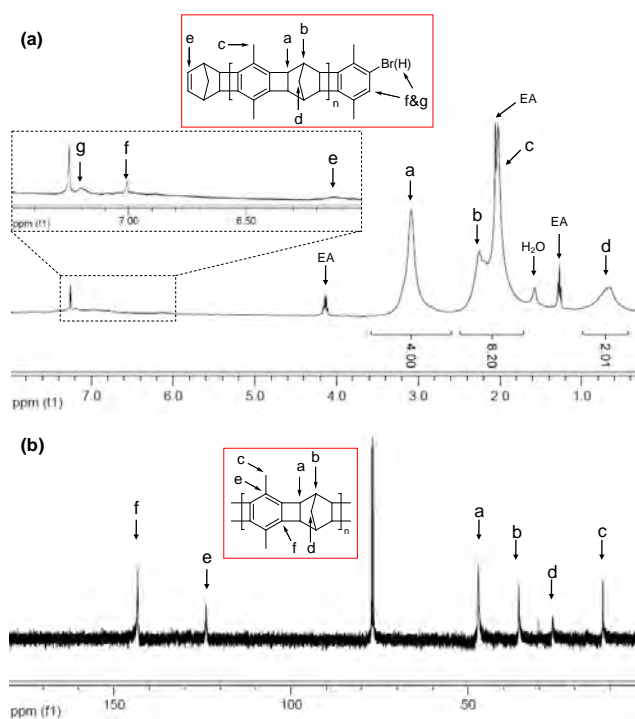


entry <sup>a</sup>	monomer(s)	$M_n^b$ (kDa)	PDI <sup>b</sup>	DP <sup>c</sup>
1	4a + NBD	29	1.38	150
2	4b + NBD	13	1.34	31
3	4a/4b (9:1) + NBD	16	1.58	52
4	4c + NBD	36	1.36	160
5 <sup>d</sup>	4d + NBD	13	1.66	44
6 <sup>d</sup>	4e	12	1.28	62
7 <sup>d</sup>	4f	14	1.28	91

<sup>a</sup>Reaction was conducted using 1 mol%  $\text{Pd}(\text{OAc})_2$ , 2 mol%  $\text{PPh}_3$ , 1 eq.  $\text{Cs}_2\text{CO}_3$ , [monomer] = 0.5 M in toluene at 115 °C for 24 h in a sealed tube, unless otherwise noted. <sup>b</sup>Determined by GPC MALLS analysis in THF. <sup>c</sup>Degree of polymerization =  $M_n/\text{MW}$  of repeat unit. <sup>d</sup>[monomer] = 1.0 M, reaction run for 12 h.

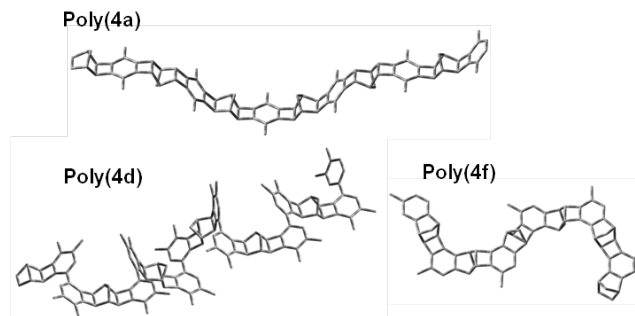


**Figure 1.** GPC traces of synthesized ladder polymers in Table 2.



**Figure 2.** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$  NMR spectra and their assignments of poly(4a) in  $\text{CDCl}_3$ .

aryl bromide. NB is a convenient reactive group that can be used for crosslinking or synthesizing block copolymers.



**Figure 3.** Simulated segment (6 repeat units) conformations of ladder polymers, poly(4a), poly(4d), and poly(4f), using molecular dynamics.

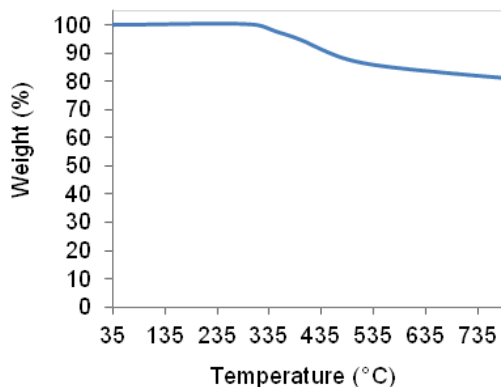
To eliminate the need for precise loading of 1:1 ratio of AA and BB types of monomers for step-growth polymerization, we also synthesized AB-type monomers **4e** and **4f** that contain NB and aryl triflate or bromide groups. Both **4e** and **4f** polymerized with no detectable monomer remaining and produced the expected ladder backbones as indicated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Their polymerizations needed to be stopped after 12 h to ensure the polymer's solubility in THF for GPC characterization.

Prolonged polymerizations of **4e** and **4f** resulted in polymers that were only soluble in chloroform, which presumably had higher MW. Interestingly, monomer **4f** induces a fixed bending angle of  $\sim 120^\circ$  at each repeating unit of **poly(4f)**, resulting in a kinked ribbon backbone conformation (Figure 3). The kinked ribbon backbone results in a more expanded conformation. This was evidenced from comparing the GPC traces of **poly(4e)** and **poly(4f)**, which have similar absolute MW and PDI ( $M_n=12$  and 14 kDa, respectively), but **poly(4f)** clearly shifted to an earlier elution time (Figure 1), indicating its larger hydrodynamic volume than **poly(4e)**.

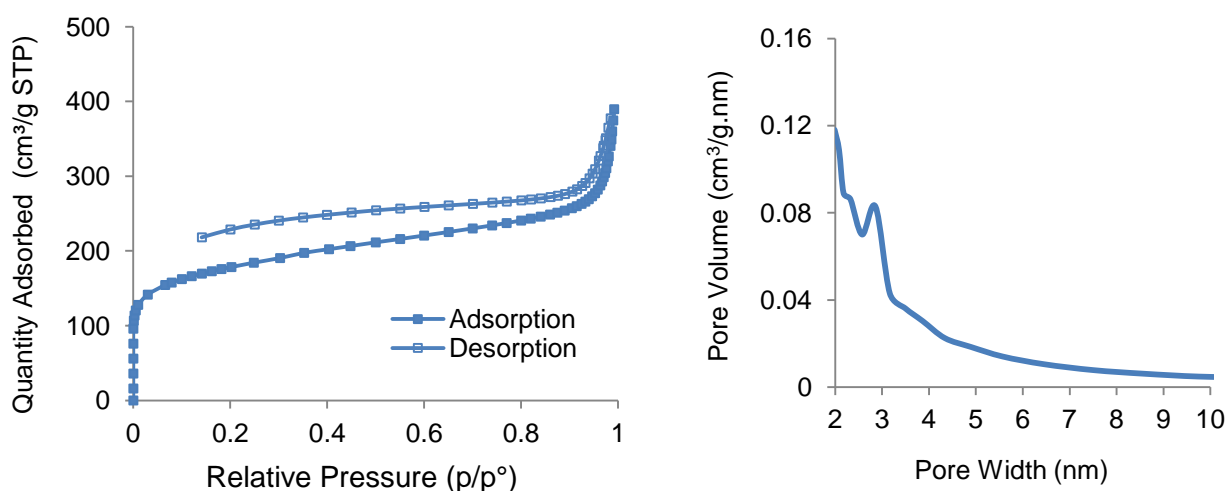
The clean chemistry also allowed us to synthesize ladder polymers with only NB end groups, when NB was intentionally used in 10 mol % excess to

can be used for crosslinking or synthesizing block copolymers. The rigid, non-conjugated ladder backbone renders these polymers interesting properties. We took polymer **poly(4a)** as an example for detailed property investigation. Differential scanning calorimetry (DSC) analysis of **poly(4a)** showed no phase transition up to  $200^\circ\text{C}$ , indicating extremely glassy backbone. Thermal gravimetric analysis (TGA) indicated that the polymer was

stable up to 315 °C, and lost only 14% weight at 496 °C, which we attributed to the loss of the two methyl substituents. Upon further heating under argon, this polymer can be carbonized with nearly 81% mass retention at 800 °C (Figure 4). In comparison, a common carbon precursor polymer, polyacrylonitrile, has a carbonization yield around 50%. The very high carbonization yield of **poly(4a)** is a result of the high degree of unsaturation of the polymer. Furthermore, frustrated packing of rigid ladder chains resulted in large intrinsic porosity with the surface area of 620 m<sup>2</sup>/g for **poly(4a)** measured by Brunauer–Emmett–Teller (BET) analysis (Figure 5). We also performed density functional theory (DFT) calculation (B3LYP/6-31G\* basis set) on the bond angle between BCB and NB motifs. The rapidly increasing energy barrier to the bond bending suggested high rigidity for the BCB linkage. The combined solubility, thermal stability, high rigidity, and large porosity may make robust BCB-NB ladder polymers promising materials for a range of engineering applications.



**Figure 4.** TGA trace of poly(4a) measured under Ar atmosphere with a heating rate of 2.5 °C/min to 800 °C.



**Figure S2.** N<sub>2</sub> adsorption and desorption isotherms for **poly(4a)** at 77 K. The BET analysis of the surface area gives 620 m<sup>2</sup> g<sup>-1</sup> and total pore volume of 0.56 cm<sup>3</sup> g<sup>-1</sup>.

## Summary

Supported by the STIR funding, we developed an efficient method to synthesize rigid ladder polymers via Pd catalyzed annulation between various readily available aryl bromides and NBD. We found blocking accessibility of other reaction pathways cleanly produced ladder polymers with rigid BCB linkage in quantitative conversions at low catalyst loading. The rigid but non-conjugated structures render good solubility of these polymers. These ladder polymers also exhibit high intrinsic porosity due to frustrated chain packing, and can carbonize to very high yield due to the high degree of unsaturation in the backbone. These unique properties will

enable a range of future applications for these polymers including membranes for separation, dielectric materials, and precursors to carbon materials.

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